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EXPERIMENTAL EVIDENCE FOR THE EXISTENCE OF HYDROPYROPE

by

Alisa Begley

A Thesis

Presented to the Graduate Committee

of Lehigh University

in Candidacy for the Degree of

Master of Science

in

Geological Sciences

Lehigh University

1985

This thesis is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science.

May 21, 1985
(date)

Charles B. Nolan
Professor in Charge

Charles B. Nolan
Chairman of Department

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ABSTRACT

The existence of a pyrope-hydropyrope series [$Mg_3Al_2(SiO_4)_3$-$Mg_3Al_2(H_4O_4)_3$] analogous to the grossular-hydrogrossular series is important because pyrope is a high-pressure candidate mineral for the upper mantle. Thus hydropyrope might be a source for water in the upper mantle. In this study, pyrope was synthesized from oxide reactants at 3.5 GPa and 1000° C in the presence of excess water. These synthetic pyropes show a 1.6% increase in lattice parameter and a 1.05% decrease in refractive index relative to the corresponding values for anhydrous pyrope synthesized from oxides in this study and as given in the literature. Infrared absorption spectra of synthetic pyrope prepared in this study reveal the presence of hydroxyl in the structure which supports the classic hydrogarnet substitution: $4H^+ \rightleftarrows Si^{+4}$. Thermogravimetric analysis and Gladstone-Dale calculations indicate substitution levels of 2.0-4.0 weight percent H_2O in pyrope synthesized in this study. This corresponds to approximately 6.7-10.0 mole percent hydropyrope substitution in pyrope. Following synthesis, hydropyrope crystals were found to be unstable at ambient conditions inasmuch as the lattice parameter and the index of refraction change spontaneously towards the normal values for synthetic anhydrous pyrope. This water loss is accelerated by heating at one

atmosphere. The phenomenon may provide an explanation for the lack of natural pyropes with a significant weight percent of water; during the rise of hydropyrope to relatively shallow low-pressure environments, the water content of natural hydropyrope is released. Now that it is known that hydroxyl can be incorporated in the pyrope structure, the magnitude of the pressure and temperature dependence of the hydropyrope substitution in pyrope should be determined experimentally.

INTRODUCTION

BACKGROUND AND PREVIOUS STUDIES

The occurrence, concentration, and mineralogical distribution of water in the earth's mantle remains an unsolved problem, the resolution of which is important in understanding the geochemistry of the mantle and magma generation. Estimates of 0.1 wt % H_2O (Wyllie, 1970), 0.2 wt % H_2O (Harris and Middlemost, 1969; Ringwood, 1966) suggest that there is an appreciable molecular proportion of water to allocate mineralogically within the mantle. Inasmuch as pyrope is a candidate mineral for the mantle (Yoder, 1976), if there is a hydropyrope series [$Mg_3Al_2(SiO_2)_3$ - $Mg_3Al_2(H_4O_4)_3$] analogous to the well-known and well-characterized hydrogrossular series [$Ca_3Al_2(SiO_2)_3$ - $Ca_3Al_2(H_4O_4)_3$], such a mineral series may serve as an important host for hydrogen and hence water in the mantle.

Hydrogarnets were first studied as an aluminosilicate mineral with a perplexing chemistry. Foshag (1920) described the new mineral plazolite, and related it to sodalite. However, subsequent studies indicated that the structure of plazolite and an earlier described mineral, hibschite (Cornu, 1906), were closely related to ugrandite garnet (Winchell, 1933). Delving into the chemistry and structure of these minerals, Pabst (1937) concluded, upon examination of x-ray powder diffraction patterns,

that plazolite and grossular garnet were isostructural and that the formula for plazolite is: $Ca_3Al_2(SiO_4)_2(H_4O_4)$. Belyankin and Petrov (1941) and Pabst (1942) studied these minerals in further detail and suggested that the substitution, (H_4O_4) (SiO_4), was responsible for this hydrogarnet. A hydrothermal synthesis and x-ray powder diffraction study of the garnet-hydrogarnet series (Flint et al., 1941) led to the conclusion that a complete solid-solution series exists between grossularite and hydrogrossular and between andradite and hydroandradite. Hydrogrossular, however, was the only silica-free garnet which was synthesized (Flint et al., 1941).

More recent research has concentrated almost solely on synthetic hydrogrossular. Cohen-Addad et al. (1964) and Cohen-Addad (1969) used neutron powder diffraction, nuclear magnetic resonance methods, and infrared absorption spectroscopy and reported that there are OH^- groups in synthetic hydrogrossular. Therefore, the mechanism by which a hydrogarnet is formed appears to be the substitution of four hydrogen ions for one silicon ion: $4H^+ \rightleftarrows Si^{+4}$ (Cohen-Addad et al., 1964). Hydrogrossular is isostructural with grossularite; both have space group symmetry Ia3d (Cohen-Addad et al., 1964). A refinement of the hydrogrossular structure was completed using a deuterated hydrogrossular, $Ca_3Al_2(D_4O_4)_3$ (Foreman, 1968).

Previously, the terms hydrogrossular and hydrogarnet were used interchangeably. Now however, it is becoming increasingly apparent that natural and synthetic hydrogarnets exist with a wide range of composition. Therefore, the general formula for a hydrogarnet is: $X_3Y_2(SiO_4)_{3-p}(H_4O_4)_p$ with $0 \leq p \leq 3$. This formula maintains X as the eight-coordinated cation and Y as the six-coordinated cation. The hydrogen content of a garnet is commonly reported as weight percent H_2O. However, the H_2O does not occur as a molecular group (Meagher,1982). The hydrogarnet structure is revealed in the hydrogrossular structure (Foreman, 1968; Cohen-Addad, 1968, 1969). The four hydrogen ions that charge balance each missing silicon ion lie outside of the tetrahedron as defined by the four oxygen ions. This forms a (H_4O_4) tetrahedron that has larger dimensions than the normal anhydrous tetrahedron, (SiO_4) in garnet. In the solid solution series, with an increasing wt % H_2O, or, in other words, with an increasing H^+ content, garnet exhibits a significant change in physical properties. As the H^+ content increases, the unit-cell edge (a) characteristically increases and the refractive index (n_D) decreases (Meagher, 1982).

In addition to the extensive study of the hydrogrossular series, other natural hydrogarnets have been analyzed including hydroandradite (Peters, 1965), hydrospessartine, hydroandradite, hydrogrossular and hydropyrope (Wilkens and Sabine, 1973), as

well as pyralspite garnets (Aines and Rossman, 1984b). The results have ranged from 10.9 wt % H_2O for plazolite, a member of the hydrogrossular series, to 0.009 wt % H_2O for pyrope (Wilkens and Sabine, 1973). Aines and Rossman (1984b) have found that garnets of the natural pyralspite series commonly contain hydrogen. The reported substitution ranges from 0.02 - 0.25 wt % H_2O. Following the successful synthesis of silica-free hydrogrossular (Flint et al., 1941), the synthesis of several other hydrogarnets has been attempted. Ito and Frondel (1967) successfully synthesized intermediate members of the hydroandradite series; Matthes (1961) and Hsu (1968, 1980) successfully synthesized intermediate members of the hydrospessartine series; Ackermann et al. (1983) reported the high-pressure synthesis of minor amounts of hydropyrope substitution in pyrope.

OBJECTIVES OF THIS STUDY

Many models of the mineralogical composition of the mantle have been proposed (Ringwood, 1966, 1970; Wyllie, 1970; Yoder, 1976). These models are in accord with the view that the mineralogy of the mantle varies with depth, or, in other words, changes with increasing pressure. Experimental and geophysical evidence suggest that the upper mantle is composed of peridotite with inclusions of eclogite and dunite. With increasing depth,

this is transformed to spinel peridotite. At depths of 50-75 km the spinel peridotite is transformed to garnet peridotite (Wyllie, 1970) which persists to depths of 350-400 km. The garnet peridotite has been described (Yoder, 1976) as a plum-pudding mixture with pyrope and clinopyroxene constituting plums sitting in a pudding of orthopyroxene and olivine.

Water appears to be a significant constituent of the mantle. It has been proposed (Ringwood, 1966) that the interior of the earth contains up to five times the amount of water that is in the present day hydrosphere. The importance of water on processes including magma generation has been clearly established (Yoder and Tilley, 1962). Water may be held in the mantle as a grain boundary film between anhydrous phases (Wyllie, 1970) or in various hydrogen bearing species, or both. Several high-pressure hydrous phases have been synthesized (Ringwood and Major, 1967; Bauer and Sclar, 1981) that may prove important. Sclar et al. (1967) synthesized a possible H-bearing pyroxene. Considering the substitution that forms a hydrogarnet ($4H^{+} \rightleftarrows Si^{+4}$), a significant question arises. Is the pyrope of the garnet peridotite of the mantle a hydropyrope? If so, pyrope could play a prominent role in the storage of water in the mantle. Schreyer and Seifert (1969) found hydrous breakdown products at temperatures within the stability field of pyrope. One of their explanations is that the pyrope grown at relatively low

temperatures (800°-850° C) is a hydropyrope. Aines and Rossman (1984b) analyzed numerous natural pyralspite garnets including several that were 90% pyrope using single-crystal infrared spectroscopy. Their results indicate that anhydrous pyralspite garnets are the exception. Almost all the garnets they examined contained some water in the form of the hydrogarnet substitution.

The present study was proposed to assess whether hydropyrope could be synthesized within the stability field of pyrope, which was established by Boyd and England (1957). The stability limits of pyrope lie within mantle conditions (Wyllie, 1970), and, therefore hydropyrope may be considered as a potential stable phase within the mantle. In addition to high-pressure synthesis, an attempt was made in this study to delineate the pressure-temperature stability field of hydropyrope.

EXPERIMENTAL METHODS

PREPARATION AND ANALYSIS OF STARTING MATERIALS

The materials used in the synthesis of pyrope and hydropyrope were carefully selected high-purity reagents.

Magnesium oxide

Magnesium oxide powder (periclase) was supplied by Spex Industries, Inc. (lot #07781). The sample purity was given as 99.999 wt % MgO. This material was prepared for high-pressure experimentation by heating at 1000° C for two hours to remove any traces of surface-held H_2O or $Mg(OH)_2$. Each heat-treated batch was then cooled and stored in a desiccator. Petrographic and x-ray powder diffraction analysis showed that this material was single-phase periclase.

Aluminum oxide

Finely divided aluminum oxide powder (corundum) was supplied by Spex Industries, Inc. (lot #09801). The sample purity was given as 99.998 wt % Al_2O_3. This material was prepared for high-pressure experimentation by heating at 750° C for 24 hours to remove any traces of surface-held H_2O or $Al(OH)_3$. Each treated batch was then cooled and stored in a desiccator. Petrographic

and x-ray powder diffraction analysis showed that this aluminum oxide powder was single-phase corundum.

Silica

Pure anhydrous silica was prepared from reagent grade silicic acid powder supplied by Spex Industries, Inc. (lot # 08771). The sample purity was given as 99.9999 wt % SiO_2. This material was prepared for high-pressure experimentation by heating at 1000° C for 12 hours to remove any combined or surface held H_2O. At temperatures above 1100° C cristobalite formed from the silicic acid. The dehydrated material was cooled and stored in a desiccator. Petrographic and x-ray powder diffraction analysis showed that the silica, heat treated at 1000° C, was amorphous.

Water

The water (H_2O) used in the high-pressure experimental runs was distilled and deionized and then stored in tightly capped vials. The water was boiled immediately prior to use to remove dissolved CO_2.

Oxide Mixtures

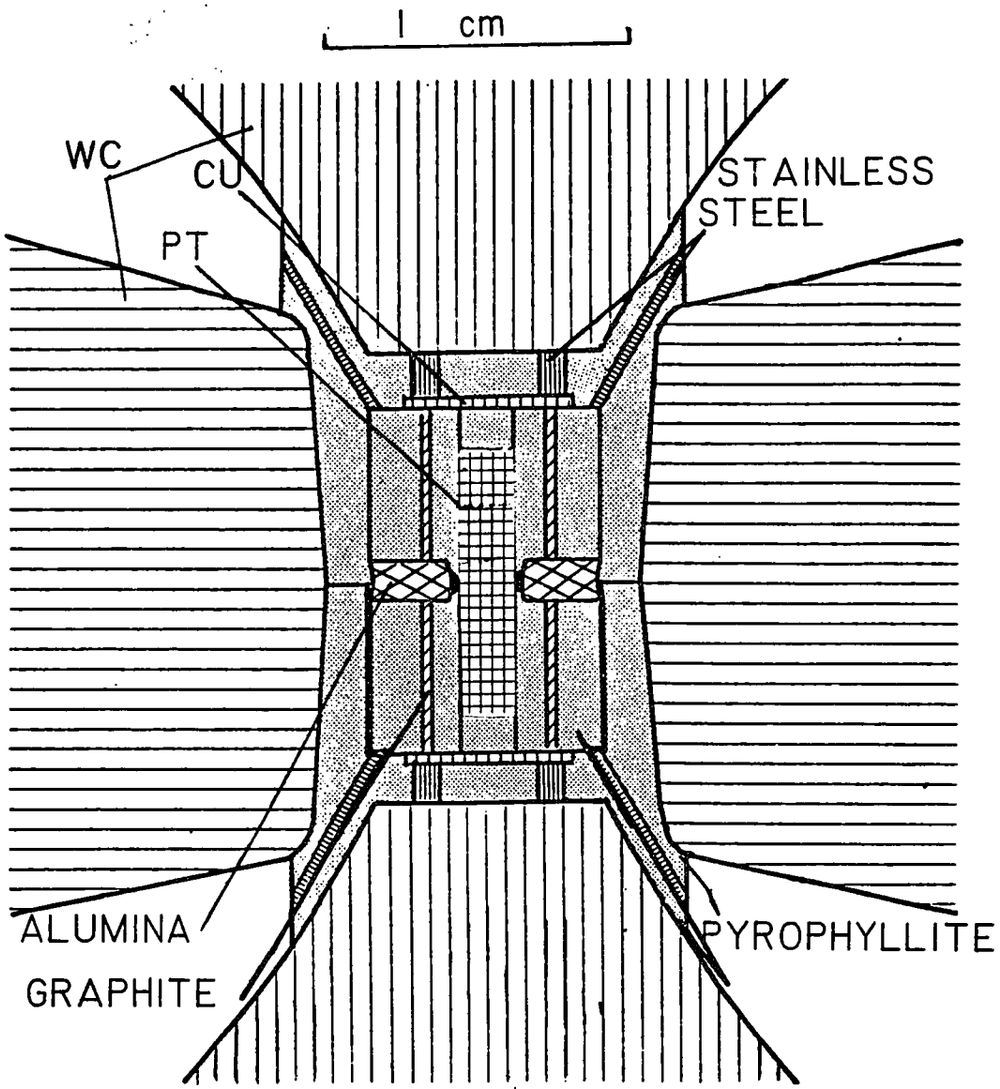
Both the stoichiometric and the non-stoichiometric pyropic oxide mixtures that were used in the high-pressure experiments

were prepared from their respective oxide components. The mixing was done in a Diamonite mortar which was first ground with fine-grained corundum and then ultrasonically cleaned and dried. Prepared amounts of each component in the experimental mixture were first weighed to the nearest $\pm$ 0.01 mg. These individual components were then mixed in the mortar and ground under acetone for approximately 15 minutes. The mixture was dried at 110° C for 12 hours and then examined petrographically to determine maximum particle size. The mixture was then stored in a desiccator.

HIGH-PRESSURE HIGH-TEMPERATURE EXPERIMENTS

Experimental equipment

The experimental device used in the high-pressure synthesis of pyrope and hydropyrope was a modified version of the "Belt" (Hall, 1960). The design of the belt permits the simultaneous application of high-pressure and sustained high-temperature to the sample. The apparatus is capable of generating 6.0 GPa and a concomitant internal steady-state temperatures up to 1500° C. The basic features of the belt are illustrated in Figure 1. The pressure is achieved by advancing two truncated variable-angle conical tungsten carbide pistons (diameter of the flat face is 9.5 mm) into a sample volume bounded and supported laterally by a



THE BELT APPARATUS

FIGURE 1 Cross section of the Belt apparatus

toroidal tungsten carbide die. The die and the pistons are each supported by three concentric interference-fit steel rings which effectively compress the tungsten carbide prior to pressure loading of the sample. Surrounding the outer steel ring is a hollow brass race through which water is circulated during an experimental run in order to cool the steel rings and tungsten carbide parts thereby increasing their effective strength while the sample is at high temperature. The pressure seal is maintained by two sets of nested conical pyrophyllite gaskets separated by a thin steel cone. These specially machined gaskets thermally and electrically insulate the sample volume.

In an experimental run, the sample is placed within the gasketing which is then placed in the toroidal die assembly. The sample assembly within the toroidal die is placed on the lower piston; the outer edges of the die assembly, the steel and hollow brass rings, are supported by three sections of a rubber O-ring. The lower piston is raised to meet the upper fixed piston with a commercial 100-ton hydraulic press. This not only pressurizes the sample but also completes the electrical circuit for the internal steady-state resistance heating of the sample. The pressure on the sample is a direct function of the ram force applied as recorded by the pressure on the hydraulic fluid in the press. The internal pressure is calibrated as described later.

The elevated temperature to which the sample is subjected during an experimental run is produced by passing a high current at low voltage through a cylindrical axial resistance heater of graphite. When the sample is under compression, the electrical current passes from one piston through the graphite heater to the other piston to complete the circuit. Power to the circuit is controlled by manually setting a Variac autotransformer tap connected in series with a voltage step-down transformer. The temperature of the sample under compression was monitored by feeding the EMF output of an internal thermocouple simultaneously to a digital millivoltmeter and a strip chart recorder. Thermocouple reference-junction compensation was provided externally by a calibrated electronic millivoltage cold junction compensator. At 1000° C the temperature was controlled to within $\pm$ 10° C.

Calibration and determination of sample pressure

The pressure applied to the sample within the die assembly is monitored by relating the applied ram force as calculated from the readings on a conventional hydraulic gauge to an internal electrical-resistance scale based on fixed points on the absolute high-pressure scale. The calibration is made by determining the ram force necessary to cause discontinuities in electrical resistance of certain well-characterized metals. Accurate values

of these pressure-induced electrical discontinuities at 25° C for certain high-purity metals are given by Hall (1971). The following metals were chosen to fix the calibration scale within the pressure range required to synthesize pyrope:

Bismuth I-II at 2.550 ± 0.006 GPa

Thallium II-III at 3.67 ± 0.03 GPa

Barium I-II at 5.5 ± 0.2 GPa

The calibration scale was determined by placing each metal in the sample assembly and compressing it incrementally with the hydraulic press while monitoring the resistance with a Kelvin bridge.

Pressure-induced discontinuities for each metal were clearly resolved on a plot of electrical resistance vs. ram force. The transitions took place over a finite range; however, the midpoint was taken as the value for the discontinuity. The calibration curve for the "belt" apparatus used in these experimental runs could then be constructed as shown in Figure 2.

Sample assembly

The sample assembly in these experiments was designed specifically to hold water throughout the high-pressure high-temperature experimental run. A capsule was formed from Pt tubing (0.120" outside diameter with 0.006" wall) and Pt end caps (3/32" and 1/8" diameters) punched from 0.005" thick Pt sheets.

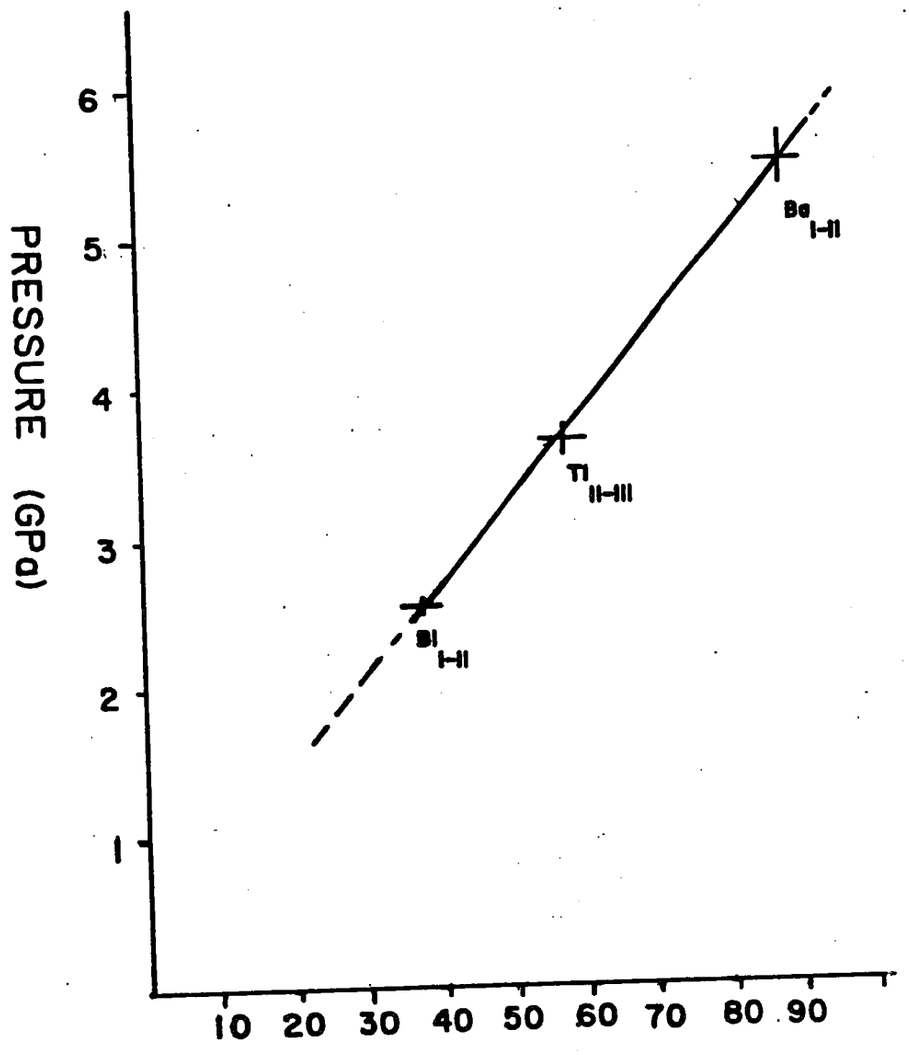


FIGURE 2 Pressure Calibration

Pressure calibration curve as used for the "belt" in the this study. The length of the arms of the crosses represent the error limits.

A completed capsule is shown in Figure 3. The tubing was cut into 0.275" lengths. These lengths of tubing and the caps were ultrasonically cleaned, washed, and dried. The larger caps (1/8" diameter) were shaped so they were slightly bowed. The shaped cap fit just inside the end of the tubing with both edges aligned. This outer end cap was then welded to the tubing to form a closed end in the following manner. The ground of a DC carbon arc welder was fixed to a copper block and the capsule was held with an alligator clip at the positive end of the arc welder. A slight touch of the capsule to the copper block formed a clean weld. The smaller Pt cap (3/32" diameter) was dropped inside next to the outer cap to add strength to the capsule during axial compression. The sample charge was loaded into the partially completed capsule in the following manner. The prepared powdered oxide mix was poured into the open end of the capsule, and then tamped until the tube was uniformly one-half full. Water was next measured and added with a calibrated microsyringe. The remainder of the oxide mix was poured and tamped until the charge filled the tube. A small inner end cap covered the charge and the outer shaped cap was placed on top. Another contact weld sealed the charge in the capsule.

The capsule was placed inside a pyrophyllite cylinder. Two caps of pyrophyllite were fixed at each end of the cylinder, completely encasing the capsule in pyrophyllite. Three co-axial

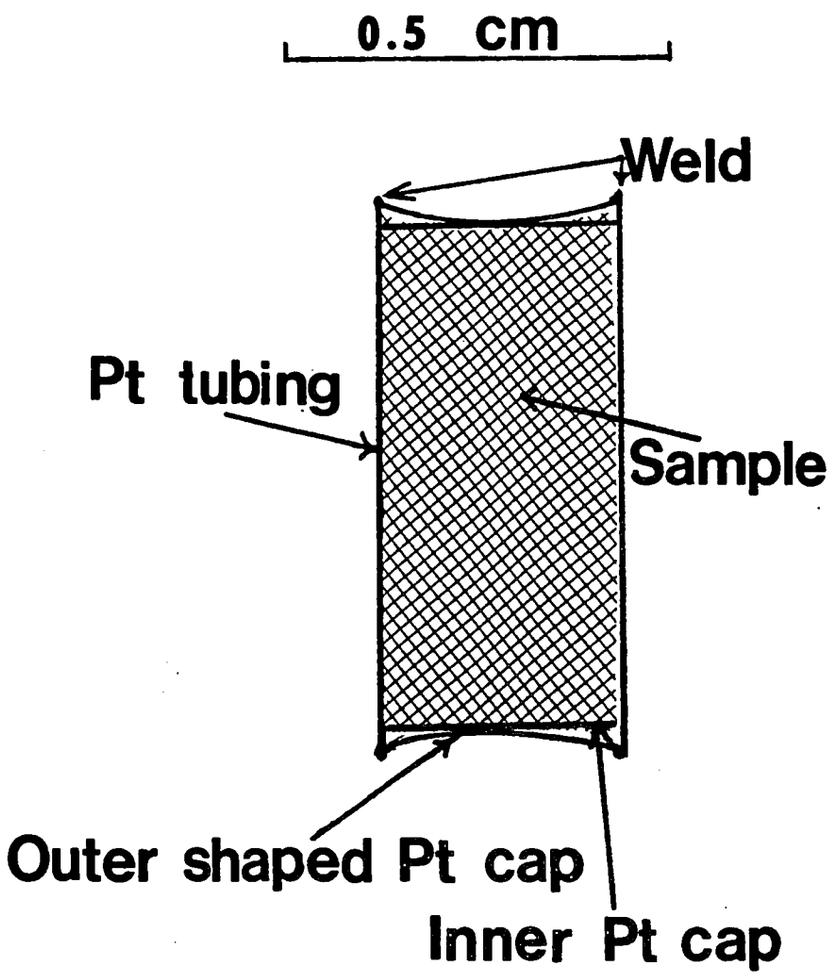


FIGURE 3 Cross Section of Sample Capsule

cylinders and the extension of the outer conical pyrophyllite gaskets separated the capsule from the toroidal tungsten carbide die. Two of these cylinders were machined from pyrophyllite which was then dehydroxylated by heating to 800° C for 4 hours. The gaskets provide quasi-hydrostatic pressure conditions around the sample and serve as electrical insulation for the resistance heating circuit. Fitting snugly between the two dehydroxylated pyrophyllite cylinders is a thin-walled sleeve of spectrographic grade graphite which serves as the resistance heater. Electrical contact with the heater tube is made by means of two copper discs, one at each end of the cylinder. A steel ring in each of the inner conical gaskets completes the electrical circuit from one piston through the graphite cylinder to the other piston.

Two separate Platinum vs. Platinum-10% Rhodium thermocouples were used during each run to measure the temperature of the capsule. Two thermocouples were needed due to the frequent failure of the thermocouple lead wires during an experimental run. The "spare" thermocouple proved invaluable until a reliable power-temperature curve was established. Each thermocouple was made by point welding 0.010" diameter Pt and Pt-10% Rh wires. The ends of the wires were inserted through a twin-bore dense alumina sheath (0.15" long and 0.062" outside diameter). The alumina shielded the wires from each other and the graphite heater tube. The brittle alumina was coated with a mixture of 2

parts Ceramabond 305 (manufactured by Aremco Products, Inc., Ossining, N.Y.) and 1 part hexagonal boron nitride. Under pressure, this material flowed into any fractures which developed in the alumina sheath and thus maintained the electrical insulation of the thermocouple wires. The thermocouples were inserted into holes drilled radially through the pyrophyllite cylinders and the graphite heater, midway between the axial ends. The wires were drawn out through V shaped grooves carved in the outer pyrophyllite cylinder. The completed sample assembly was placed inside the sample volume as defined by the toroidal tungsten carbide die. The steel cone separating the nested conical pyrophyllite gaskets for the upper piston were replaced by six strips of steel to insure a non-interfering EMF (Figure 4). In the spaces between steel strips, the wires were coiled to prevent breakage during axial compression. The inner conical gasketing for the upper piston was placed on top of the sample assembly and the thermocouple wires were carefully drawn out between the lateral supporting O-ring pieces, to the external readout circuitry.

Run Procedure

The previously described sample assembly fits within the toroidal die. The die and surrounding rings form a "pancake" which is placed on the lower piston. The desired pressure for

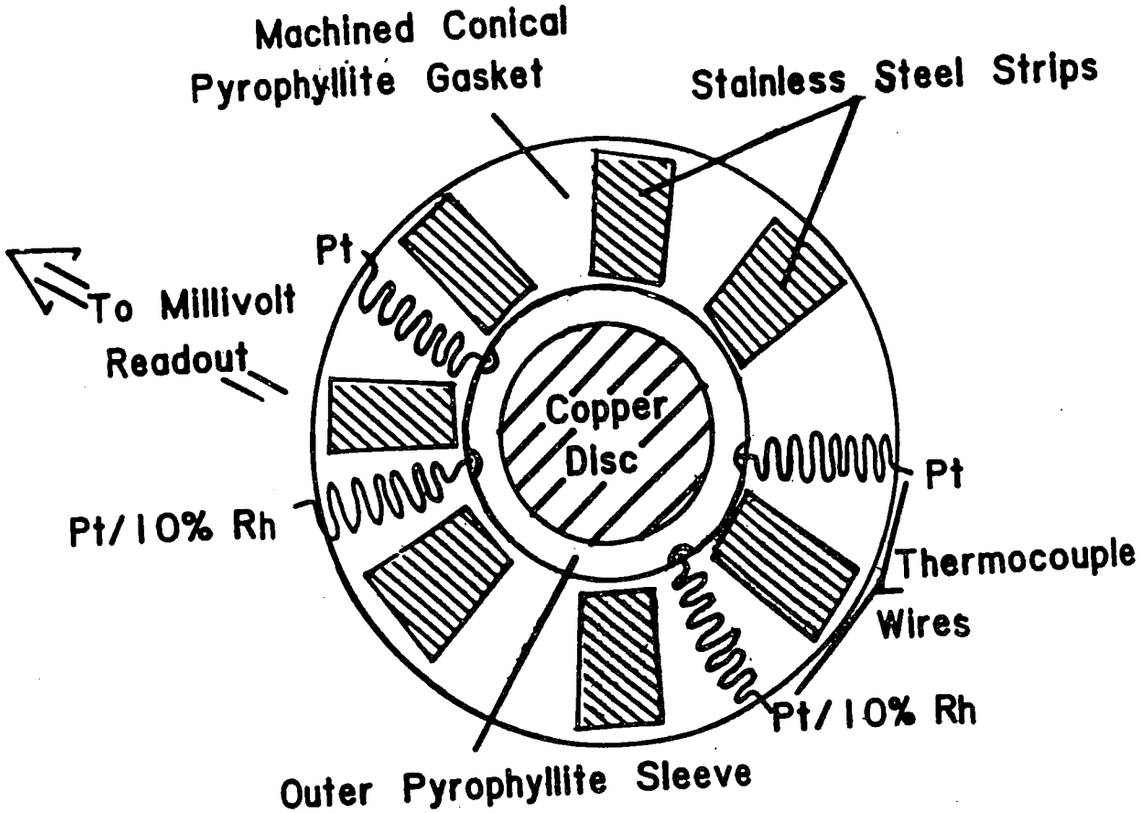


FIGURE 4 5 mm

Top view of sample assembly
showing location of thermocouple wires

the experimental run was reached by incrementally increasing the ram force over a period of two hours. This lengthy time period allowed for the proper extrusion of the pyrophyllite gaskets and the formation of a uniform pressure seal. Once the appropriate pressure was reached, the temperature was incrementally increased over a period of 30 minutes. The target pressure and temperature conditions were maintained for an attempted minimum of one hour. This one-hour interval was initially a random choice which later proved more than adequate for pyrope crystals to nucleate and grow. The sample was next isobarically quenched by cutting the power to the resistance heater. The quench rate as indicated on the strip-chart recorder was approximately 500 $^{\circ}$ C/sec. Once quenched, the pressure on the sample was released, and the capsule was removed from the gasketing. The capsule was sliced open longitudinally with a razor blade and the contents examined. Water retention in the capsule was established through the direct observation of water droplets or vapor cavities inside the capsule.

ANALYTICAL PROCEDURES

PETROGRAPHIC ANALYSIS

The product of each run was initially examined with a standard petrographic microscope. The number and identity of phases present and overall grain size were established. Conventional grain mounts in an oil with index of refraction 1.700 were used for this initial examination. Grain size, although usually exceedingly small, was occasionally up to 0.3 mm. The larger grains commonly showed the typical dodecahedral morphology of garnet.

Following a confirmation of crystalline phases using x-ray powder diffraction analysis, the pyrope was petrographically examined again. The index of refraction (n_D) of each synthetic pyrope was determined by means of the immersion method using sodium light. Due to their high density and short shelf life, the oils used in the determination of n_D of the synthetic garnet were checked with an Abbe refractometer to assure an accurate determination of n_D for the synthetic crystals.

X-RAY POWDER DIFFRACTION ANALYSIS

X-ray powder diffraction was used to confirm the petrographic observations and to determine the lattice parameter (a) of the synthetic garnet. The Debye-Scherrer method was

employed using a 114.6 mm camera and CuK_{α} radiation. The exposure time was typically 20 hours. The film was read to obtain 2θ and d-spacing values for identification purposes. The 2θ values for garnet were indexed; lattice parameters were refined by means of a computer based least-squares refinement program (Appleman et al., 1973).

INFRARED ABSORPTION SPECTROSCOPY

Selected samples of synthetic hydropyrope were analyzed by infrared absorption spectroscopy. This was done to confirm the hydrogarnet substitution in the synthetic hydropyrope. Samples chosen were those with the most enlarged unit-cell edge (a), on the assumption that these samples would show the most well defined peaks attributable to OH^-. The potassium bromide pressed-pellet technique was the method of sample analysis. Approximately 1 mg of garnet was ground in a mortar and then mixed with approximately 200 mg of dried (450° C, 48 hours) spectrographic grade powdered KBr (supplied by Matheson, Coleman and Bell, Inc.). Every effort was made to prevent exposure of the dried KBr to atmospheric H_2O, including the period required for formation of the pellet immediately prior to infrared spectroscopy. Pellets were formed by squeezing 50 to 100 mg of sample mix in a mechanical press. Air in the sample chamber, however, was not evacuated. Samples were scanned in the range

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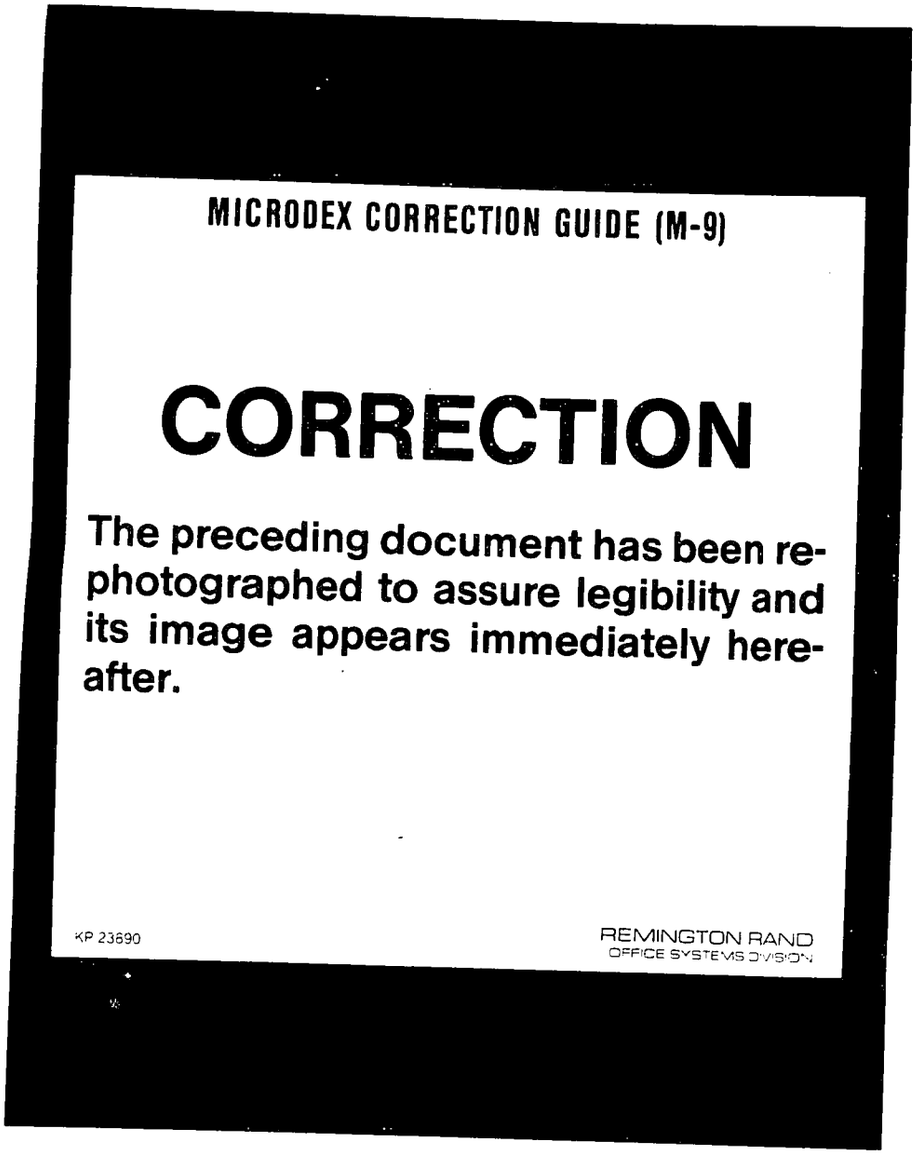

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4000 cm^{-1} to 500 cm^{-1}. A minimum of 75 background scans were stacked and stored and a minimum of 75 scans of the pellet were stacked and stored. A computer subtraction resulted in the final spectrum which was examined for the OH^- vibrational frequencies which would confirm the hydrogarnet substitution. Only qualitative infrared absorption analyses of these spectra were carried out; no attempt was made to quantify the intensity of the appropriate absorption bands with respect to the concentration of OH^- in the solid sample.

RESULTS

EXPERIMENTAL PRODUCTS

Twenty-two controlled high-pressure high-temperature experiments were run in this study. The conditions and products of each run are listed in Table 1. The results of these runs can be grouped into five general categories: experimental failure, non-stoichiometric runs, low-temperature runs, pyrope, and hydropyrope. Each is described below.

Experimental failure

The runs which have no product listed (runs #1, #4, #6, #10 in Table 1) are the result of experimental failure. The loss of quasi-hydrostatic pressure, for example, can result in the failure of the capsule walls. The quasi-hydrostatic pressure of the sample environment can be lost if the gaskets are not uniform in grain size and texture and free of flaws, or if there are any voids in the sample assembly. The radially drilled holes for insertion of the thermocouples were the most frequent cause of the loss of hydrostatic pressure. The loss of hydrostaticity results in axial compression supported by the 0.006 " walls of the capsule. If these walls fail, the sample charge and the Pt of the capsule mix with gasket material. Nothing can be determined from such a product. Another kind of experimental

TABLE I CONDITIONS AND RESULTS OF EXPERIMENTS

RUN #	P	T	X	TIME	PRODUCTS
# 1	2.5 GPa	1000° C	$3MgO + Al_2O_3 + 3SiO_2 + H_2O$	90 min.	NO CAPSULE
# 2	2.5 GPa	600° C	$3MgO + Al_2O_3 + 3SiO_2 + H_2O$	45 min.	Sudoite
# 3	3.0 GPa	1200°C	$3MgO + Al_2O_3 + 3SiO_2 + H_2O$	60 min.	Hydropyrope + Glass
# 4	2.5 GPa	1200° C	$3MgO + Al_2O_3 + 3SiO_2 + H_2O$	60 min.	NO CAPSULE
# 5	2.5 GPa	200° C	$3MgO + Al_2O_3 + H_2O$	15 min.	Brucite + Spinel
# 6	2.5 GPa	100° C	$3MgO + Al_2O_3 + H_2O$	10 min.	NO CAPSULE
# 7	2.5 GPa	1000° C	$3MgO + Al_2O_3 + SiO_2 + H_2O$	45 min.	Spinel + Hogbomite + Pyrope
# 8	2.5 GPa	1000° C	$3MgO + Al_2O_3 + 3SiO_2 + H_2O$	120 min,	Hydropyrope + Hectorite + Saponite
# 9	3.0 GPa	500° C	$3MgO + Al_2O_3 + SiO_2 + H_2O$	30 min.	Spinel + Lizardite
# 10	3.0 GPa	100 C	$3MgO + Al_2O_3 + H_2O$	10 min.	NO CAPSULE
# 11	3.5 GPa	800° C	$3MgO + Al_2O_3 + H_2O$	60 min.	Brucite + Spinel

TABLE I Continued

RUN #	P	T	X	TIME	PRODUCTS
# 12	3.5 GPa	1000° C	$3MgO + Al_2O_3 + 2SiO_2 + H_2O$	60 min.	Pyrope + Hydrogrossular
# 13	3.5 GPa	1000° C	$3MgO + Al_2O_3 + 2SiO_2 + H_2O$	60 min.	Pyrope + Hydrogrossular
# 14	3.5 GPa	900° C	$3MgO + Al_2O_3 + 3SiO_2 + D_2O$	20 min.	Pyrophyllite + Kyanite + Akdalaite
# 15	3.5 GPa	850° C	$3MgO + Al_2O_3 + 3SiO_2 + D_2O$	60 min.	Kyanite + Talc + Staurolite + Enstatite
# 16	3.5 GPa	1100° C	$3MgO + Al_2O_3 + 3SiO_2 + D_2O$	60 min.	Hydropyrope
# 17	3.5 GPa	1250° C	$3MgO + Al_2O_3 + 3SiO_2$	45 min.	Anhydrous Pyrope
# 18	3.5 GPa	1000° C	$3MgO + Al_2O_3 + 3SiO_2 + D_2O$	10 min.	Hydropyrope
# 19	? GPa	1100° C	$3MgO + Al_2O_3 + 3SiO_2 + D_2O$	30 min.	Ellestadite + Surinamite
# 20	3.5 GPa	900° C	$3MgO + Al_2O_3 + 3SiO_2 + H_2O$	30 min.	Talc + Corundum + Ringwoodite
# 21	3.5 GPa	850° C	$3MgO + Al_2O_3 + 3SiO_2 + H_2O$	20 min.	Talc + Corundum + Ringwoodite
# 22	3.5 GPa	1150° C	$3MgO + Al_2O_3 + 3SiO_2 + H_2O$	60 min.	Hydropyrope

failure occurred when the upper piston failed and the pressure on the sample could not be determined (run #19). It is probable that the sample pressure was less than the minimum pressure required to be in the stability field of pyrope based on the nature of the experimental products. Experimental failure occurred a total of five times during this study.

Non-stoichiometric runs

All hydropyropes synthesized in this study were grown from a stoichiometrically balanced oxide mixture. Silica-deficient deviations from this balanced mixture (runs #5, #7, #9, #11, #12, and #13 in Table 1) produced what appear to be other stable phases, such as spinel.

One comment should be made in reference to runs #12 and #13. These were originally just one mole deficient in silica. However, some contamination with Ca^{+2} occurred. These runs produced zoned garnets; hydrogrossular in the core and pyrope on the rims as shown by microprobe analysis.

Low-temperature runs

There are runs in which hydropyrope did not form from an oxide mixture of garnet stoichiometry (runs #2, #14, #15, #20 and #21 in Table 1). These runs coincide with the lower experimental temperatures, in the range of 500°-900° C. In this study,

pyrope did not nucleate unless the temperature at high pressure was at least 1000° C.

Pyrope

Anhydrous pyrope was synthesized in this study (run #17 in Table 1) from a stoichiometric anhydrous oxide mixture. All of the physical properties used for identification of anhydrous pyrope correlate exactly with those values given in the literature (Fleischer et al., 1984) (Table 2).

Hydropyrope

Hydropyrope was synthesized in five runs (runs #3, #8, #16, #18 and #22 in Table 1). Identification of hydropyrope was based on the magnitude of the lattice parameter (a) and the index of refraction (n_D). The values of these physical properties for synthetic hydropyrope are compared with the values of synthetic anhydrous pyrope in Table 2.

These five synthetic hydropyrope samples deviate from the reported values of a and n_D for synthetic pyrope, and these deviations can be attributed to the hydrogarnet substitution in pyrope. In the hydrogarnet substitution, four OH^- groups substitute for one SiO_4 tetrahedron (Cohen Addad et al., 1964; Foreman, 1968). The four protons lie outside of the tetrahedron as defined by the oxygen ions. This substitution causes a change

GARNET	n_D	a, Å	MOLE % HYDROPYROPE
From Skinner, 1956	1.714	11.46	0
RUN # 3	1.696	11.647	10
RUN # 8	1.704	11.646	6.7
RUN # 16	1.696	11.609	10
RUN # 17	1.714	11.453	0
RUN # 18	1.698	11.581	6.7
RUN # 22	1.698	11.576	6.7
$Mg_3Al_2(SiO_4)_2(H_4O_4)_4$	1.670★	11.699★	33.3
$Mg_3Al_2(H_4O_4)_3$	1.586★	12.15★	100

★ Calculated using Vegard's Law and data from Flint et al, 1941

TABLE 2 Physical Parameters of Synthetic Hydropyrope

Unit cell edge is given to within ± 0.002 Å.

in the physical parameters α and n_D. Meagher (1982), Hsu (1980) and Flint et al. (1941) all confirm that the hydrogarnet substitution follows Vegard's Law, i.e. a linear relationship exists between lattice parameters and composition of solid solutions when the composition is expressed as an atomic or mole percentage. Therefore, the data in Table 2 suggests the presence of hydropyrope substitution. Flint et al.(1941) demonstrated experimentally and Meagher (1982) supported theoretically that a decrease in n_D with increasing hydrogarnet substitution occurs in this series. The hydropyropes synthesized in the this study all show a decrease in n_D relative to the normal anhydrous value.

DISCUSSION

The results of this study clearly indicate that pyrope with some substitution of hydropyrope has been synthesized. Each hydropyrope shows the deviations in α and n_D from those of anhydrous pyrope which are expected as a result of the hydrogarnet substitution in pyrope. All hydropyropes synthesized in this study were grown by reaction of oxide mixtures with garnet stoichiometry at 3.5 GPa and a minimum of 1000° C in the presence of either H_2O or D_2O.

INFRARED ABSROPTION SPECTRA

Recent investigations of infrared spectra of natural hydrogarnets (Aines and Rossman, 1984a) delineate the range 3700-3400 cm^{-1} as the key to identification of the hydrogarnet substitution. Anhydrous garnet spectra are featureless in this region whereas hydrous garnet spectra are characterized by multiple absorption bands within this region. The chemistry of the hydrogarnet determines the position of these multiple bands (Aines and Rossman, 1984b). Variations in the spectra due to the identity of the eight-coordinated cation have been clearly established. The end-member pattern of pyrope, however, is not well established because of the rarity of an occurence of end-member pyrope in nature.

Two peaks appeared consistently in the OH^- region of the infrared spectra of the synthetic hydropyropes prepared in this study (Figure 5). One is located near 3430 cm^{-1} and the other is near 3600 cm^{-1}. Aines and Rossman (1984b) place the generalized peaks for OH^- vibrations in pyrope at 3575 cm^{-1} and 3690 cm^{-1}. Although the peak locations are noticeably different for this study, the "typical" spectra reported by Aines and Rossman (1984b) are not of end-member pyrope.

Infrared spectra of the synthetic hydropyrope prepared in this study reveal the classic hydrogarnet substitution, that of $4H^+ \rightleftarrows Si^{+4}$. The spectrum of hydropyrope of run #8 (Figure 5) is markedly different from the spectrum of anhydrous pyrope of run #17 (Figure 6). There are two peaks in the spectrum for run #8 within the OH^- region, and the remaining peaks, between 1200 cm^{-1} and 500 cm^{-1} coincide with those of run #17 for anhydrous pyrope (Farmer, 1974). The two broad peaks, one at wavenumber 3430 cm^{-1} and one at wavenumber 3600 cm^{-1}, clearly indicate the presence of OH^- vibrations in these synthetic hydropyropes. Zabinski (1966) studied thoroughly the infrared spectra of hydrogarnets. Zabinski's spectra (1966) display well-defined sharp peaks for the hydrogarnet substitution. In the present study, however, substitutional levels were far below those of the hydrogrossular (6 wt % H_2O) studied by Zabinski (1966). The hydrogarnet region for natural pyropic spectra reported by Aines and Rossman (1984b)

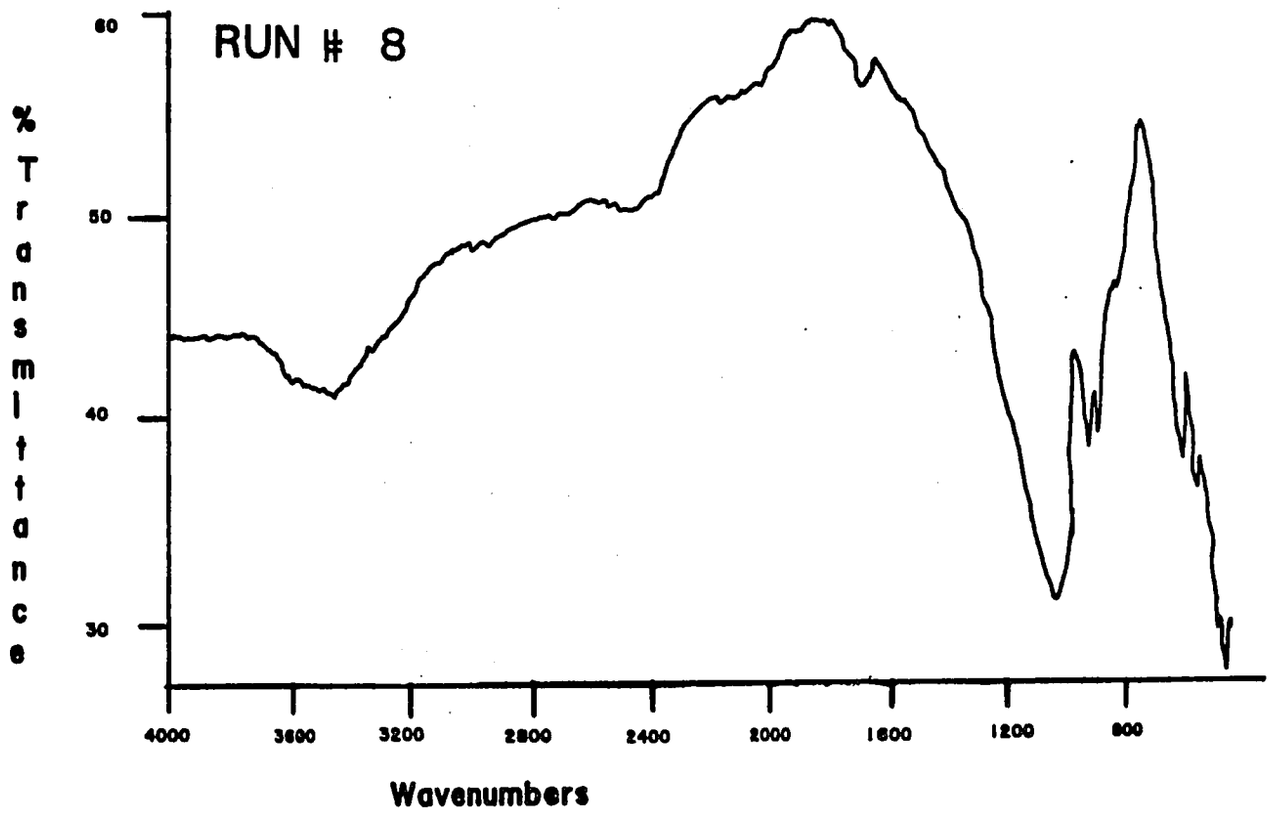

FIGURE 5 INFRARED ABSORPTION SPECTRUM

Infrared Absorption Spectrum for hydropyrope of Run #8.

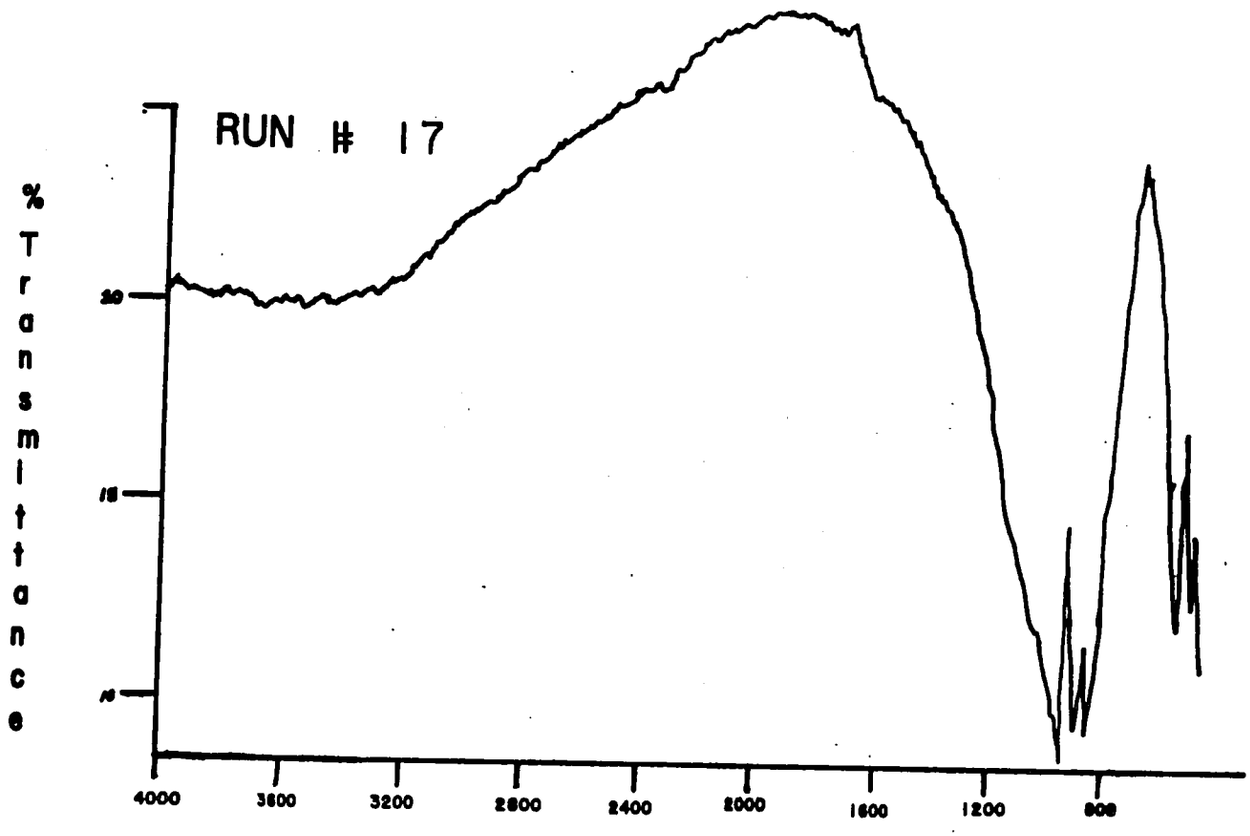

FIGURE 6 INFRARED ABSORPTION SPECTRUM

Infrared Absorption Spectrum for anhydrous pyrope of Run #17.

have much broader absorption bands corresponding to lower levels of hydrogarnet substitution, and these broad peaks are similar to those of the synthetic samples of this study. The spectra in Figures 5 and 6 indicate the presence of hydropyrope; the hydrogarnet region contains two broad peaks in the spectrum of run #8 whereas peaks are absent in the same region for run #17.

GLADSTONE-DALE RELATIONSHIP

The Gladstone-Dale relationship (Mandarino,1979) provides a fairly reliable check on the accuracy of the refractive index and density of the pyrope-hydropyrope series. The Gladstone-Dale relationship may also be used to calculate the density or mean refractive index of a crystalline solid. In this study, the relationship was used to calculate approximately the amount of hydrogarnet substitution in the high-pressure products.

The specific refractive energy (K) is calculated from both the chemical composition and the physical properties of the mineral. Ideally the physical (calculated from measured physical properties) and chemical (calculated from chemical composition) specific refractive energies (K_P and K_C) should be equal. Therefore, the ratio K_P/K_C can serve as a measure of the combined accuracy of n_D, density (D) and the chemical composition (Mandarino, 1979).

In order to obtain reasonable values for the specific refractive energy of the intermediate-member hydropyrope synthesized in this study, the calculation of the specific refractive energy for theoretical end-member hydropyrope was completed . The theoretical value of α for end member hydropyrope was calculated using the measured percentage increase in α between grossular and hydrogrossular end members, and between andradite and hydroandradite end members (Flint et al., 1941). Both of these series show a 6.0% increase in α between the anhydrous end-member and the hydrous end-member. Therefore, a 6.0% increase was assumed for end-member hydropyrope, and this resulted in a theoretical value for α of 12.15 Å for end-member hydropyrope (Table 2). The same procedure was used to determine the value of n_D for end-member hydropyrope. This was based, however, solely on data for the grossular-hydrogrossular series; the data for the andradite series are not available in the literature.

By applying Vegard's Law, and assuming a linear relationship for α between end-member pyrope-hydropyrope compositions, a reasonable chemical formula can be deduced for each of the intermediate synthetic hydropyropes of this study. The synthetic hydropyrope of this study was placed on a Vegard plot derived from known values of α for anhydrous pyrope and theoretical values of α for end-member hydropyrope (Figure 7). Figure 7

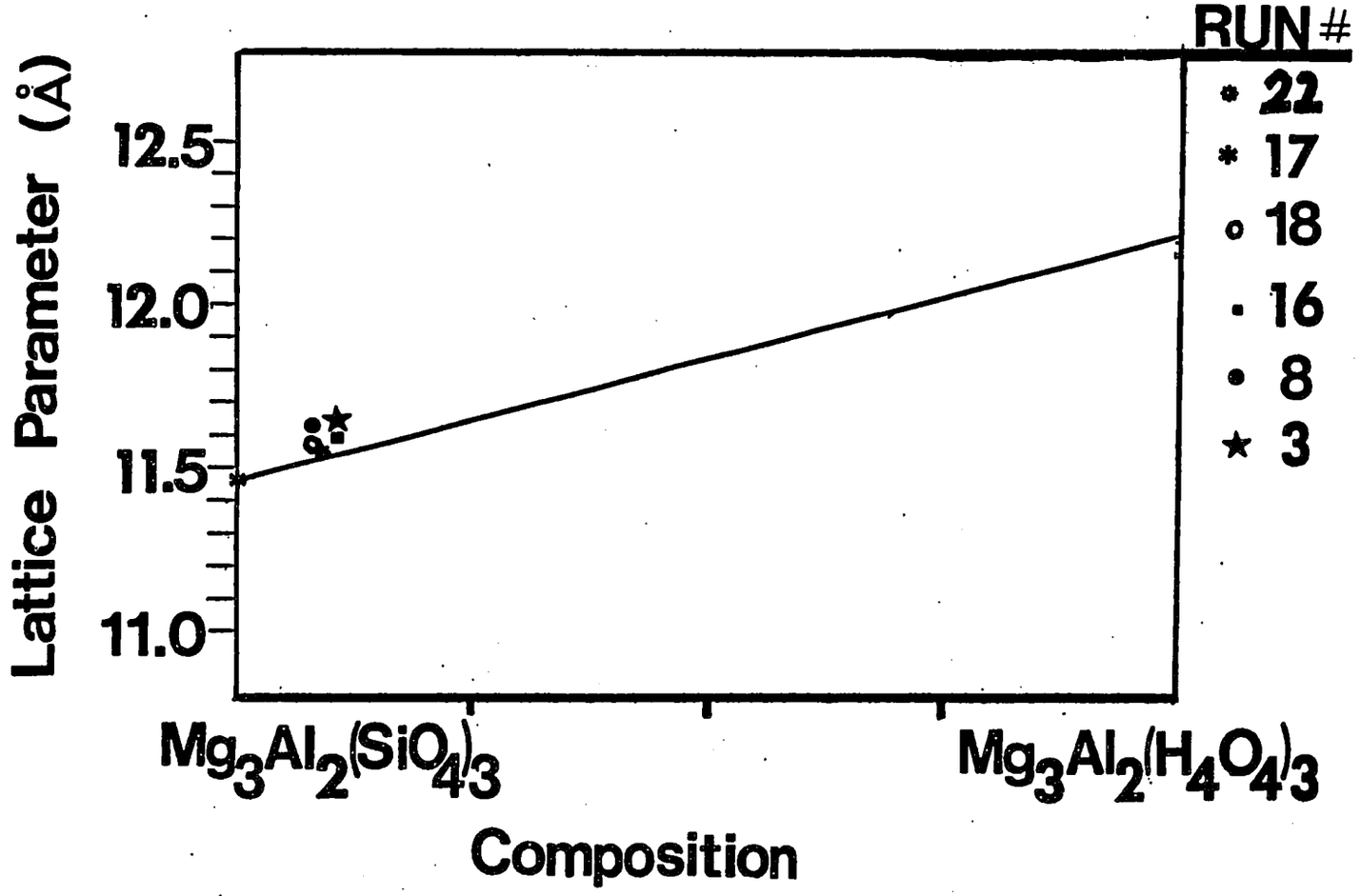

FIGURE 7 Vegard Plot of Hydropyrope of this Study

indicates a reasonable chemical composition for hydropyrope synthesized in this study. The decrease in the n_D for the pyrope-hydropyrope series was also assumed to follow a linear relationship which aided in the determination of a chemical composition for each synthetic hydropyrope. The density for each synthetic hydropyrope was calculated from its estimated chemical formula using the following equation:

$$D = \frac{(\text{Mol wt}) \times Z}{(\text{Avg \#}) \times (a)^3}$$

Mol wt= the molecular weight of the estimated chemical composition

Z = the number of formulas in a unit cell of hydropyrope

Avg # = Avagadro's number

This calculated density was used in the calculation of K_P.

$$K_P = \frac{n_D - 1}{D}$$

The same estimated chemical composition provided the weight percentage of each oxide constituent for the calculation of K_C of the corresponding hydropyrope.

$$K_C = \Sigma \frac{k_i p_i}{100}$$

k_i = specific refractive energy constant of each oxide constituent

p_i = weight percent of each oxide constituent

The values of K_P and K_C were calculated from the derived chemical formulas, the specific refractive energy constants of Mandarino (1976) and the measured values of α and n_D for each hydropyrope and for synthetic anhydrous pyrope.

The estimated chemical formulas and the resulting ratios (K_P/K_C) for synthetic anhydrous pyrope and each synthesized hydropyrope are given in Table 3. The accuracy of the combined data is scaled according to the magnitude of the deviation from unity for the ratio K_P/K_C (Mandarino, 1979) (Table 4). The approximate weight percent of H_2O in each hydropyrope synthesized in this study can be calculated from the estimated chemical formula (Table 5). The Gladstone-Dale relationship thus offers a fairly simple check to these derived chemical compositions. The well-established data for anhydrous pyrope yields a K_P/K_C ratio that falls into the excellent category according to Mandarino's (1979) criteria, whereas all of the derived chemical compositions fall into the superior category of Mandarino (1979). Although the Gladstone-Dale calculations alone do not prove the validity

GARNET	K_P	K_C	K_P/K_C
Anhydrous pyrope From Skinner, 1956	0.1993	0.2053	1 - 0.029
Anhydrous Run #17	0.2003	0.2053	1 - 0.024
Theoretical: $Mg_3Al_2(SiO_4)_2(H_4O_4)$	0.2131	0.2177	1 - 0.021
RUN #3: $Mg_3Al_2(SiO_4)_{2.7}(H_4O_4)_{.3}$	0.2091	0.2089	1 + 0.001
RUN #8: $Mg_3Al_2(SiO_4)_{2.8}(H_4O_4)_{.2}$	0.2104	0.2077	1 + 0.013
RUN #16: $Mg_3Al_2(SiO_4)_{2.7}(H_4O_4)_{.3}$	0.2083	0.2089	1 - 0.003
RUN #18: $Mg_3Al_2(SiO_4)_{2.8}(H_4O_4)_{.2}$	0.2062	0.2077	1 - 0.007
RUN #22: $Mg_3Al_2(SiO_4)_{2.8}(H_4O_4)_{.2}$	0.2059	0.2077	1 - 0.009

TABLE 3 Values Calculated for the Gladstone-Dale Relationship

K_P / K_C =	
1 ± 0.000-0.019	SUPERIOR
1 ± 0.020-0.039	EXCELLENT
1 ± 0.040-0.059	GOOD
1 ± 0.060-0.079	FAIR

TABLE 4 Criteria for Accuracy of K_P and K_C

(Mandarino, 1979)

FORMULA	SiO_2	H_2O
$Mg_3Al_2(SiO_4)_3$	44.71%	—
$Mg_3Al_2(SiO_4)_{2.8}(H_4O_4)_{0.2}$ ★	42.235%	1.809%
$Mg_3Al_2(SiO_4)_{2.7}(H_4O_4)_{0.3}$ ★★	40.974%	2.730%
$Mg_3Al_2(SiO_4)_2(H_4O_4)$ ★★★	31.699%	9.504%

★ RUN #8, #18, #22
★★ RUN #3, #16
★★★ THEORETICAL

TABLE 5 WEIGHT % OF SILICA AND WATER IN SYNTHETIC HYDROPYROPE

of the calculated chemical compositions, the ratio K_P/K_C does strongly support the conclusion that intermediate members of the hydropyrope-pyrope series were synthesized.

SPONTANEOUS DEHYDRATION

An x-ray powder diffraction pattern of run # 3 was made one year after synthesis. The refined lattice parameter, a, was 11.46 Å as compared with the initial a (11.64 Å) of the product. These results suggest that the initial hydropyrope spontaneously lost water at room conditions and reverted to anhydrous pyrope. Hydropyrope, therefore, is apparently unstable at earth-surface conditions of pressure and temperature. A time vs. a study was made by re-examining the hydropyropes using x-ray powder diffraction (Debye-Scherrer methods) each month. The same crystals were analyzed each time; the x-ray pattern was indexed, and a refined value of a was obtained as a function of time since synthesis (Figure 8). The resulting curve indicates that water was released spontaneously throughout the eight month interval of study. In addition, the n_D of the crystals was determined once each month. The increase in the value of n_D also supports the interpretation that water was lost from the initial hydrogarnet; the n_D increased to the anhydrous value during the eight-month study. Thus the changing a and n_D indicate that the intermediate members of the hydropyrope-pyrope series synthesized at high

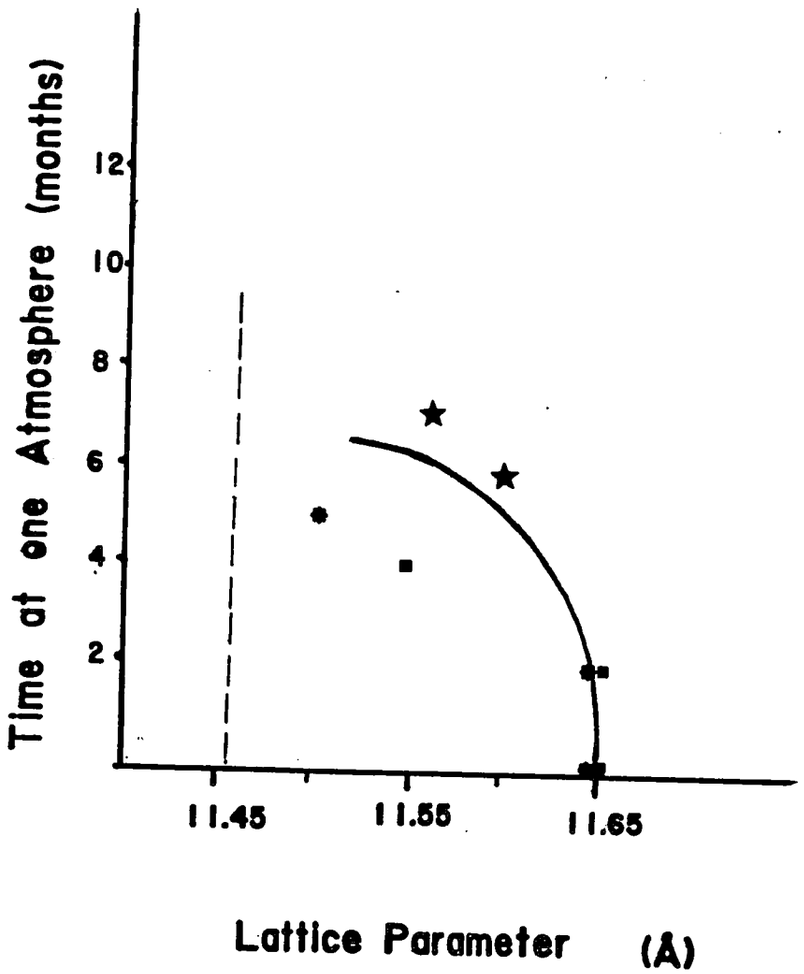

FIGURE 8 Lattice Parameter vs. Time Since Synthesis

pressure in this study is unstable at room conditions. The original values of α and n_D of the high pressure garnet changed to those of anhydrous pyrope within one year following synthesis while "sitting on the laboratory shelf". This phenomenon provides an explanation for the lack of hydropyrope substitution in natural garnets. Natural pyropic garnets generally contain less than 0.22 weight percent H_2O (Aines and Rossman, 1984b), whereas those synthesized in this study appear to contain close to 2.7 weight percent of H_2O, a much greater percentage. Thus the magnitude of the hydrogarnet substitution in these synthesized pyropes results in an unstable garnet at room temperature and pressure.

With the realization that the spontaneous loss of water could be an important factor in the stability of hydropyrope, the phenomenon of water loss was accelerated by heating the hydropyrope for predetermined time periods at various temperatures at one atmosphere. After heating, a Debye-Scherrer pattern was obtained from each sample, and a refined lattice parameter determined; the n_D for each heat-treated hydropyrope was also measured. The results indicate that the hydropyrope was dehydrated during heating (Figure 9). While heating the hydropyrope at 200° C for 48 hours, half of the substituted H_2O is released according to the decrease in the unit cell edge, assuming a Vegard relationship for the pyrope-hydropyrope series.

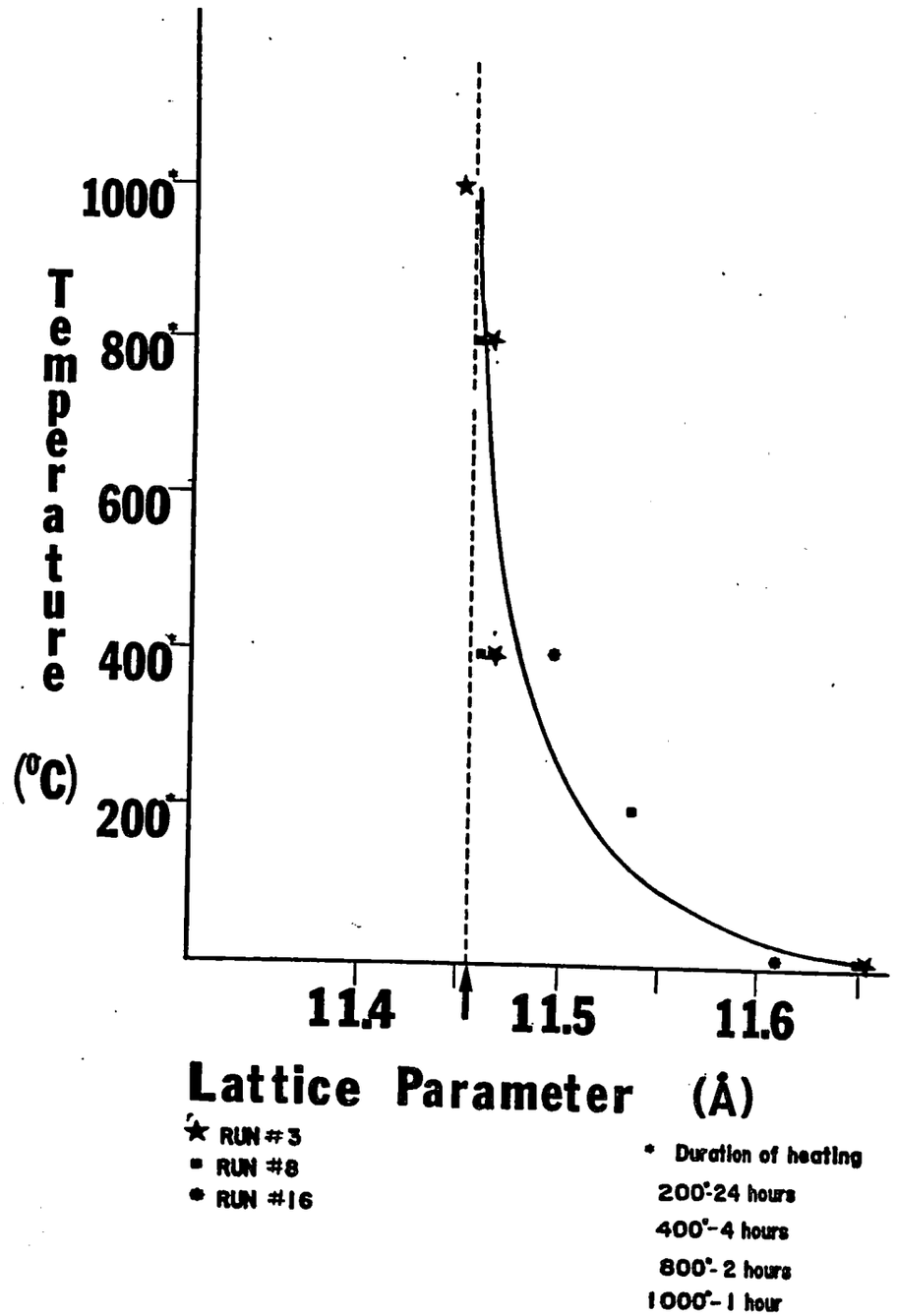

FIGURE 9 Lattice Parameter vs. Temperature of Heating

The amount of H_2O released is increased when the same sample is heated to 400° C for 4 hours. Futhermore, all of the H_2O is released when this sample is heated at 1000° C for just one hour. The α of the crystals of hydropyrope after heat-treatment at 1000° C corresponds to the α of anhydrous pyrope. These dehydrated crystals also show a simultaneous increase in the index of refraction. This approach to the values for α and n_D of anhydrous pyrope must have been a result of the loss of H_2O from the hydropyrope.

The following reaction is proposed for the dehydration of end member hydropyrope:

$$Mg_3Al_2(H_4O_4)_3 \rightarrow 6H_2O + Mg_3Al_2O_6$$

Although $Mg_3Al_2O_6$ is not a known phase, this chemistry can also be written as $2MgO + MgAl_2O_4$, which are the known phases periclase and spinel. A silica deficient or low-silica phase is expected as the water is released from intermediate members of the pyrope-hydropyrope series. Every effort was made to determine whether a new phase nucleated during the dehydration of hydropyrope. When examined with a petrographic microscope, the heated crystals did reveal a foreign substance within thermal-stress cracks; however, the amount of this material was insufficient for identification. Debye-Scherrer patterns did not reveal any substance other than pyrope.

The water content of newly synthesized hydropyrope can be accurately measured by thermogravimetric analysis (TGA). This technique involves a measure of the weight loss of the sample as a function of temperature. A TGA curve was completed for hydropyrope of run #22 (Figure 10) within 36 hours after synthesis. The temperature was increased at the rate of 10° C/min to a final temperature of 1000° C. The resulting pattern illustrates the dynamic loss of water from hydropyrope. There is no indication of a threshold temperature above which water is released. Rather, water was released throughout the analysis. The sample used for this TGA pattern was not pre-dried, and therefore, the total observed weight loss of 2.5 wt % is considered to be the sum of the weight of the (H_4O_4) tetrahedra within hydropyrope and the weight of the water adsorbed or otherwise weakly bound to the surface of the sample.

The rate of weight loss for the sample varies as a function of temperature. The initial rate, 0.6 wt %/100° C, slows at 350° C to a rate of just 0.05 wt %/100° C. Some of this initial weight loss may be due to molecular water held on the surface of the sample. The slower rate continues until the sample reaches a temperature of 750° C, at which time the rate increases to 0.3 wt %/100° C. Both rates, 0.05 wt %/100° C and 0.3 wt %/100° C, of weight loss can be attributed solely to the dehydration of hydropyrope. This TGA curve suggests a weight loss upon

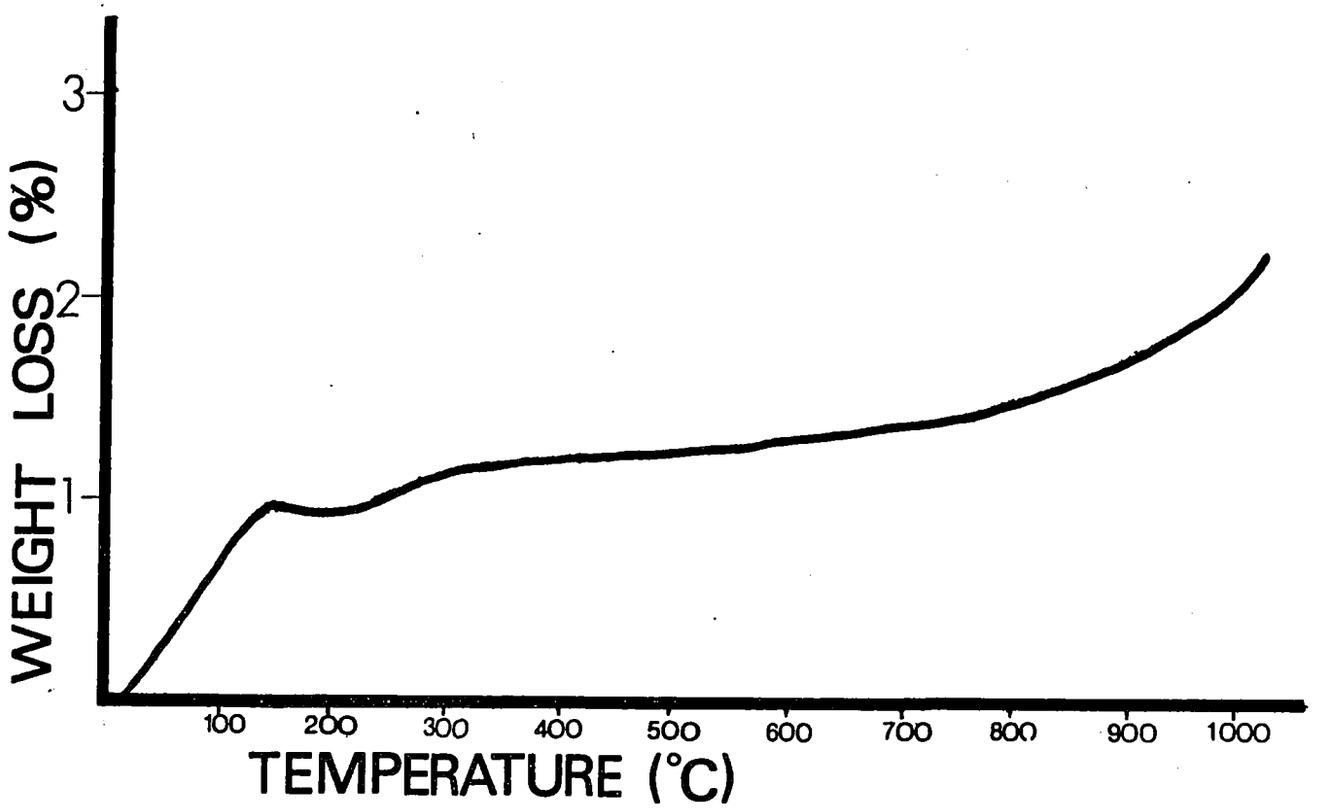

FIGURE IO THERMOGRAVIMETRIC CURVE

dehydration of 2.5 % for run #22. If some of the initial weight loss (through to 150° C) is attributed to surface held water the remaining weight loss, 1.5 wt %, can be attributed to dehydration of hydropyrope.

The rate of weight loss at the termination of this TGA had not slowed or leveled off, therefore the lattice parameter of run #22 was determined following the TGA. The resulting a, 11.49 Å, indicated that the sample was not completely dehydrated. Inasmuch as TGA is a dynamic process, the same sample was heated again at 1000° C for an hour and x-rayed again. This time the lattice parameter showed that the sample was completely dehydrated, and the additional weight loss calculated from the change in a was 0.8%. Therefore, the weight loss as determined by TGA represents a minimum weight loss for run #22. Allowing 1.0 wt % for the evaporation of surface water indicates a minimum weight loss of 1.5 wt % solely due to dehydration of the hydropyrope of run #22 during TGA. Additional weight loss during the second heating, at 1000°, suggests a total weight loss of 2.3 wt % for the hydropyrope of run #22. This compares with an approximation for run #22 of 1.8 wt % water based on the Gladstone-Dale relationship. Gladstone-Dale approximations and the TGA pattern collected for run #22 suggest a minimum of 6.7 mole percent substitution hydropyrope in pyrope.

GEOLOGIC IMPLICATIONS

Pyrope is a pressure-dependent phase which is stable only above 2.0 GPa (Boyd and England, 1957). Therefore, the potential hydrogarnet substitution in pyrope is of significance with respect to understanding both the petrology and geophysical properties of the upper mantle. In particular, this has a bearing on the depth to which water could be chemically bound in solids and the conditions under which that water would be liberated. This study has shown that hydropyrope can be synthesized at high pressure and that it can hold and store significant quantities of water within upper-mantle conditions of temperature and pressure. Hydropyrope will release its water upon the decrease of pressure and continued high temperatures.

Natural pyrope has previously been considered to be essentially anhydrous (Wilkens and Sabine, 1973). The theoretical rejections for hydropyrope have been two-fold. The first argument against hydropyrope focuses on the enlarged molar volume associated with hydrous garnets (Meagher, 1982). Pyrope, as a high-pressure phase, should not be favored with an increase in lattice parameter (Martin and Donnay, 1972). It has been suggested, however, that the (H_4O_4) tetrahedron might actually be more compressible (Fyfe, 1970). If the H^+ bonds were to become symmetrical, a considerable shortening of the O-O distance would

follow. In this case, a hydrogarnet might be favored at high-pressure. Hence, hydropyrope might be favored in the mantle. The second negative theoretical argument against the existence of hydropyrope was proposed by Zabinski (1966). Zabinski (1966) stated the bond length for Mg-O in pyrope is much longer than the average length for a silicate. This bond length is increased in the case of a hydrogarnet and would ultimately cause hydrous pyrope to be an unfavored phase at high pressure. This study has shown, however, that hydropyrope can be synthesized at high pressure.

This study also indicates that hydropyrope can be synthesized with a significant weight percent of water. The hydrous component was incorporated into the pyropic garnet structure at temperatures and pressures simulating upper mantle conditions. If hydropyrope is stable in the mantle, it could provide a mechanism for storing water in the earth at great depths. The breakdown of amphiboles at pressures greater than 2.5 GPa had previously limited the occurrence of chemically bound water in amphiboles to depths no greater than 100 km. Hydrogarnet substitution in pyrope permits the occurrence of chemically bound water in the mantle to depths of at least 100 km and depths which are limited only by the ultimate high-pressure breakdown of hydropyrope which is not known at present. Water

incorporated into pyrope by the hydrogarnet substitution may be stable at depths as great as 300-400 km.

In addition to the stability at high pressure of hydropyrope, this study also revealed that hydropyrope is inherently unstable at low pressures. Hydropyrope rapidly releases the structurally bound water at elevated temperatures and low pressures and spontaneously releases its water over time at room conditions. Water has been shown experimentally to have a profound effect on lowering the temperature required for generation of basaltic magma (Yoder and Tilley, 1962). Perhaps water released during the breakdown of hydropyrope might aid in the generation of magma. The water released by hydropyrope may thus contribute to magma generation in the upper mantle.

Recently, natural pyropic garnets from mantle-derived kimberlites and basalts have been found to contain water at concentrations much lower than those of this study (Aines and Rossman, 1984b). The decrease in pressure and the continued high temperatures during the ascent of magmas to the surface would result in the release of most if not all of the structurally bound water in hydropyrope. Garnets found at or near the surface of the earth following these processes, have a much lower weight percent of water than the hydrogarnets initially recovered in this study (0.02-0.25 vs. 1.8-2.7 wt % water). Natural near-surface garnets of mantle origin may have lost most of the water

originally substituted in their structure during emplacement in the crust.

Lastly, studies of kimberlite-related mantle nodules suggest the presence of a metosomatizing fluid under mantle conditions, but the source of such fluids is not obvious (Dawson, 1980). Perhaps the source of the metosomatic fluids is hydropyrope from which water has been released.

Hydropyrope might play an important role in the storage and release of water in the upper mantle. Hydropyrope freshly recovered from high-pressure experiments in this study shows that significant amounts of water are stable in the pyrope structure through the hydrogarnet substitution mechanism. This substitution level, however, is unstable at room pressure and temperature and the hydrogarnet spontaneously releases the chemically bound water over time.

CONCLUSIONS

This study has shown that the classic hydrogarnet substitution, $4H^{+} \rightleftarrows Si^{+4}$, can occur in pyrope. This substitution forms a potential solid-solution series [$Mg_3Al_2(SiO_4)_3$-$Mg_3Al_2(H_4O_4)_3$], analogous to the well-characterized solid-solution series grossular-hydrogrossular [$Ca_3Al_2(SiO_4)_3$-$Ca_3Al_2(H_4O_4)_3$]. The pyrope-hydropyrope solid-solution series is stable at high pressures and high temperatures. Although an end-member hydropyrope was not synthesized in this study, intermediate members of the potential solid-solution series were prepared. The hydropyrope was characterized on the basis of physical-property deviations from those of anhydrous pyrope, infrared spectra, and dehydration of the hydropyrope. Infrared spectra display OH^{-} vibrations which confirm the hydrogarnet substitution in pyrope. The calculated Gladstone-Dale relationship supports the conclusion that intermediate members of the pyrope-hydropyrope series were synthesized. A thermogravimetric analysis indicates minimum substitution levels of 2.3 wt % H_2O were synthesized in this study. This weight percent of H_2O substitution corresponds to approximatley 10 mole % hydropyrope.

The stability of hydropyrope is limited to high pressures. At room pressure the hydropyrope spontaneously releases the water

of the hydrogarnet substitution. This phenomenon is accelerated at room pressure and high temperatures.

Hydropyrope is proposed as a stable water-bearing candidate mineral within the upper mantle which, based on experimental synthesis conditions, may be stable to depths as great as 300 km. Intermediate members of the hydropyrope-pyrope series may store significant quantities of water in the upper mantle.

Additional experimental work is needed to establish and define limits on the extent of the hydrogarnet substitution in pyrope as a function of both pressure and temperature. Efforts to synthesize end-member hydropyrope have thus far been unsuccessful in a pressure range limited to 3.5 GPa.

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VITA

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